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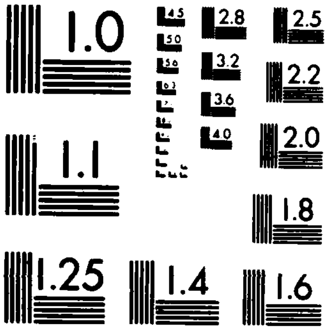

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REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER Technical Report No. 8	2. GOVT ACCESSION NO. AD-A137216	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Vibrational Spectroscopy of Acetylene Decomposition on Palladium (111) and (100) Surfaces		5. TYPE OF REPORT & PERIOD COVERED Interim
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) L.L. Kesmodel, G.D. Waddill, and J.A. Gates		8. CONTRACT OR GRANT NUMBER(s) N00014-80-C-0147
9. PERFORMING ORGANIZATION NAME AND ADDRESS Indiana University Foundation Department of Physics Indiana University, Bloomington, IN 47405		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Physics Program Office Arlington, VA 22217		12. REPORT DATE January 16, 1984
		13. NUMBER OF PAGES 20
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release; Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

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18. SUPPLEMENTARY NOTES

To be published in Surface Science (1984)

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Acetylene; benzene; palladium (100) and (111) surfaces; vibrational spectroscopy; electron energy loss spectroscopy; chemisorption and catalysis; thermal decomposition; CCH formation.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Vibrational spectra for thermal decomposition of acetylene (C_2H_2) on (111) and (100) surfaces of palladium obtained with high-resolution electron energy loss spectroscopy (EELS) are described. Of particular interest is the formation of CCH species on both surfaces, which are identified spectroscopically in this context for the first time. On Pd(100) CCH forms with thermal processing of chemisorbed acetylene to ~400K but on Pd(111) is co-adsorbed with a $\equiv C-CH_3$ species following 300K C_2H_2 adsorption. With

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further annealing to 450K CCH is the dominant species on both surfaces. The EELS spectra indicate that both carbon atoms are involved in the CCH interaction with the surface as implied by a C-C bond order between 1 and 2. In view of recent reports of acetylene trimerization to benzene (C_6H_6) on Pd surfaces the EELS spectra of C_6H_6 and isotopic mixtures were also analyzed but no evidence for this reaction was found.

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Contract N00014-80-C-0147

Technical Report No. 8

VIBRATIONAL SPECTROSCOPY OF ACETYLENE DECOMPOSITION ON PALLADIUM (111) AND (100) SURFACES

by

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16 January 1984

Published in Surface Sciences (1984), in press.

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Submitted to Surface Science

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triple bond (approx.)

Abstract

Vibrational spectra for thermal decomposition of acetylene (C_2H_2) on (111) and (100) surfaces of palladium obtained with high-resolution electron energy loss spectroscopy (EELS) are described. Of particular interest is the formation of CCH species on both surfaces, which are identified spectroscopically in this context for the first time. On Pd(100) CCH forms with thermal processing of chemisorbed acetylene to ~400K but on Pd(111) is co-adsorbed with a $\equiv C-CH_3$ species following 300K C_2H_2 adsorption. With further annealing to 450K CCH is the dominant species on both surfaces. The EELS spectra indicate that both carbon atoms are involved in the CCH interaction with the surface as implied by a C-C bond order between 1 and 2. In view of recent reports of acetylene trimerization to benzene (C_6H_6) on Pd surfaces the EELS spectra of C_6H_6 and isotopic mixtures were also analyzed but no evidence for this reaction was found.

1. Introduction

Recent spectroscopic studies of acetylene (C_2H_2) chemistry on palladium surfaces by several research groups [1-5] have raised many questions concerning the thermal evolution of this species. In high-resolution electron energy loss (EELS) studies on Pd(111) the formation of CCH_2, CCH_3, and CH species were detected as thermal evolution products of initially chemisorbed C_2H_2 in the temperature range 150-500K [1,2]. However, in subsequent studies with thermal desorption spectroscopy (TDS) [3-5] and ultraviolet photoemission spectroscopy (UPS) [3,4] the formation of benzene (C_6H_6) has been emphasized. Ethylene formation was also reported [4,5]. Several questions remain concerning possible C_6H_6 formation: UPS evidence [3,4] for this species is not definitive, and aspects of the TDS results are inconsistent. For example, in the study by Sesselmann et al. [3] C_6H_6 was reportedly formed only under low temperature and high exposure ($\geq$ 100L) conditions whereas Tysoe et al. [4] and Gentle and Muetterties [5] detected reactively-formed C_6H_6 at both low (230K) and high (500K) temperatures. We note that the studies in Refs. 1-4 were restricted to the (111) surface whereas (111), (100), and (110) surfaces were considered in Ref. 5.

The central issue addressed in the present work concerns the nature of acetylene-derived species present on both Pd(111) and Pd(100) surfaces in the temperature range 300-500K. In this regard the work expands on our earlier EELS studies on Pd(111) [2] and focuses on the question of C_6H_6 formation. Detailed EELS analysis of C_2H_2, C_6H_6 and their deuterated counterparts were carried out, including various isotope mixing experiments. Although a 450K acetylene-derived surface species observed on both Pd(111) and Pd(100) exhibits vibrational features similar to benzene we find that this species is, in fact, CCH. On Pd(100) the CCH species is formed near 400K from ~sp^3 hybridized acetylene. On Pd(111) both CCH and ethylidyne ($\equiv$C-CH_3) [2] are formed upon adsorption of C_2H_2 at 300K, the ethylidyne species decomposing by 450K. The Pd(100) vibrational data suggests that the CCH stereochemistry involves bonding of both carbon atoms to the surface with a bond order between 1 and 2.

Our lack of EELS vibrational evidence for benzene formation does not directly conflict with the recent studies [3-5] but rather suggests that benzene may be (i) formed in relatively small amounts on the surface or (ii) largely formed in a process leading to rapid desorption.

2. Experimental Procedures

The high-resolution electron energy loss measurements were carried out with two 127° cylindrical deflection electron spectrometers at Indiana University. The Pd(111) experiments were performed with a single-pass instrument [6] which is housed in an ion-pumped ultrahigh vacuum system (base pressure $\sim 1 \times 10^{-10}$ Torr), also equipped for ion-sputtering, low-energy electron diffraction and Auger spectroscopy. This instrument was operated at 10 meV (80 cm^{-1}) system resolution at typical elastic beam signal levels of $0.3\text{-}1.0 \times 10^{5}$ cps for hydrocarbon adsorption. The Pd(100) experiments employed a new double-pass spectrometer which achieves high signal levels at 2.5-10 meV system resolution [7]. This instrument is incorporated in a diffusion/sublimation-pumped system (base pressure $\sim 5 \times 10^{-11}$ Torr) equipped for ion-sputtering and mass spectrometry. Due to the generally low intensity of the hydrocarbon modes the spectrometer was operated at 8-9 meV (64-72 cm^{-1}) system resolution providing specular elastic beam count rates of $\sim 2 \times 10^{6}$ cps at beam energies of 4-6 eV. The high sensitivity afforded under these conditions proved valuable for detection of weak losses and facilitated off-specular measurements.

Sample preparation and cleaning for the EELS experiments has been described elsewhere [2]. High purity C_2H_2, C_2D_2, C_6H_6, C_6D_6, H_2, and D_2 gases were used and were examined with a mass spectrometer for impurities. Hydrocarbon exposures quoted in Langmuirs (1L = 10^{-6} Torr-s) were corrected for reported ion-gauge sensitivity [8].

3. Results

Extensive high-resolution EELS spectra for C_2H_2, C_2D_2, C_6H_6, and C_6D_6 on Pd(111) and Pd(100) have been obtained under various temperature and coverage conditions; isotope mixing experiments ($C_2H_2 + C_2D_2$, $C_6H_6 + D_2$, etc.) have been performed as well. In this section the salient results of this study are discussed with emphasis on (i) the possible detection of C_2H_2 trimerization to C_6H_6 and (ii) the nature of acetylene decomposition product(s) in the temperature range 300-500K.

3.1. Pd(100) vibrational spectra

The EELS spectrum for 300K adsorption of C_2H_2 on Pd(100) is shown in Fig. 1a. As discussed elsewhere [9] this spectrum is due to acetylene in a near sp^3 hybridization state as evidenced by ν_{CC} = 1210 cm^{-1} and ν_{CH} = 2920 cm^{-1}. This spectrum transforms upon warming to 450K (Fig. 1b) to one resembling those reported for CH species on (111) surfaces of Ni, Pd, Pt, and Rh [10]; characteristic is the strong CH bending loss at 750 cm^{-1} and the CH stretch at 3000 cm^{-1}. However, a broad band ca. 1340 cm^{-1} is also found which does not appreciably shift with deuteration and is, therefore, assigned to a CC stretching mode. Importantly, we find that the 750 cm^{-1}, 1340 cm^{-1}, and 3000 cm^{-1} loss intensities decay at the same rate (within experimental error of 10%) upon thermal processing from 475K to 650K. This is strong evidence that a single surface species is responsible for these modes. A likely interpretation of Fig. 1b is thus in terms of a multiply-bonded CCH species.

Figure 1c indicates that C_6H_6 formation might also provide an explanation of the 450K acetylene-derived species. Benzene adsorbed at 300K is fairly stable until ~500K with an EELS spectrum characterized by a very intense loss at 730 cm^{-1} with much weaker losses at 1130, 1440, and 3020 cm^{-1}. Quite similar spectra have been reported for C_6H_6 adsorption on Ni(111) [11,12], Ni(100) [12], Pt(111) [11], and Rh(111) [13] and consistently interpreted in terms of predominant π-bonding with the benzene ring parallel to the surface. The exceptionally strong loss at 730 cm^{-1} is assigned to the ν_4 out-of-plane CH bending mode of A_{2u} symmetry and 673 cm^{-1} frequency in the gas phase [14,15]. This mode has strong infrared activity in the gas phase and will be dipole active on the surface for parallel adsorption. The resemblance of major features of Figs. 1b,c leaves C_6H_6 formation a possibility we discuss further below.

3.2. Pd(111) vibrational spectra

EELS vibrational spectra for 150K C_2H_2 adsorption and thermal evolution were reported earlier [2]. It was found that C_2H_2 chemisorbed at 150K in an ~$sp^{2.5}$ hybridization state (Fig. 2a, ν_{CC} = 1400 cm^{-1}, ν_{CH} = 2990 cm^{-1}) and underwent hydrogenation to ethylidyne ($\equiv C-CH_3$) near 300K via a probable vinylidene ($=C=CH_2$) intermediate. Here we consider room temperature C_2H_2 adsorption at relatively low (1.5L) and higher (12L) exposures. Under these conditions a mixture of ethylidyne and CCH species form as shown in Fig. 2b,c. Ethylidyne has been characterized [2] in terms of strong modes near 1330 cm^{-1} (methyl deform.) and 1100 cm^{-1} (CC stretch). These modes are present for 300K adsorption along with the strong CH bending vibration indicative of CCH (or possibly C_6H_6). Upon warming to 500K decomposition of ethylidyne has occurred but the 750 cm^{-1} loss remains (Fig. 2d). As noted for the (100) surface this spectrum is quite similar to the EELS spectrum for associatively adsorbed C_6H_6 (Fig. 2e). Signal-to-noise levels in the Pd(111) study were not sufficient to permit conclusive identification of [illegible] loss features in the 1000-1500 cm^{-1} region for Fig. 2d,e. However, comparison of the Pd(100) and (111) spectra strongly suggests that the same acetylene-derived species is present on both surfaces at 450K. Finally, we note a 300K exposure-dependent ratio of this product and ethylidyne evident in Fig. 2b,c. This aspect will be discussed in a subsequent paper in connection with hydrogen thermal desorption results.

3.3. Off-specular analysis

In order to further explore possible detection of C_6H_6 formation selected off-specular analyses comparing C_6H_6 and the 475K acetylene-derived species were undertaken on Pd(100). As shown in Fig. 3b,c marked differences between C_6H_6 and the C_2H_2-derived species occur in the 1000-1600 cm^{-1} region. The ν_{CH} loss is also much stronger for the latter species. As shown in Fig. 3a the broad 1360 cm^{-1} band is hardly shifted upon deuteration.

These spectra indicate that the species is not benzene but rather CCH. In Fig. 3a the presence of a small amount of CCH in the CCD spectrum is evident from weak features near 750 cm^{-1} (shoulder) and 3000 cm^{-1}. Other features of note are the presence of shoulders at 850 (640) cm^{-1} in the CCH (CCD) spectra. These weaker modes may be due to the other CH bending mode (parallel to the surface plane) or to CCH species in another surface bonding configuration. The latter interpretation is consistent with the broad nature of the ν_{CC} band centered at 1360 cm^{-1}. We rule out CCH_2 or CH_2 species due to the absence of characteristic scissor vibrations (ca.1400 cm^{-1}) and on the basis of isotope mixing experiments discussed below.

3.4. Isotope mixing experiments

If the acetylene-derived species formed at 450K is C_6H_6 it is clear that mixtures of C_2H_2 and C_2D_2 will give rise to $C_6H_xD_{6-x}$ molecules with even x; the other isotopes will occur if H-D exchange occurs. Furthermore, by scaling to known gas phase frequencies for the strong ν_4 bending mode [15] reasonable predictions for the surface isotopes can be made. This mode should be dipole active in each case for parallel-bonded benzene. The various bands (ν_4) are found to occur in separated groupings [15] and the predicted surface frequencies are, for example: C_6D_6(545 cm^{-1}); sym-$C_6H_3D_3$(588 cm^{-1}); para-$C_6H_4D_2$(658 cm^{-1}); C_6H_6(740 cm^{-1}). Benzene mixtures should, therefore, be characterized by a very broad band between 545-740 cm^{-1}. Such a band was consistently produced by mixing C_6H_6 with D_2 at 150K on Pd(111) and warming to 450K. Figure 4 provides clear evidence for statistically probable $C_6H_3D_3$ or $C_6H_2D_4$ isotopes whereas C_6D_6 is largely absent as expected. Another loss appearing as a shoulder near 825 cm^{-1} is quite probably due to another strong mode for one of the isotopes [16]. These results (and similar ones for $C_6D_6 + H_2$) are qualitatively different than predictions for the CCH model which would, of course, simply give rise to the same two bands when C_2H_2 and C_2D_2 are mixed.

Isotope mixing of C_2H_2 and C_2D_2 are illustrated in Fig. 5 for Pd(100). Panel (a) shows the unreacted mixture at 300K which gives rise to two strong modes at 545 cm^{-1} and ~770 cm^{-1} upon warming to 450K. Analogous results were obtained on the (111) surface. This result clearly favors the CCH model and rules out C_6H_6 formation. In the benzene model, for example, the 770 cm^{-1} mode associated with pure C_6H_6 would have very low statistical weight for the 1:2 mixture, contrary to the EELS spectra (Fig. 5). Furthermore, we find that calibration to relative loss intensities for the separate C_2H_2 and C_2D_2 heating experiments allows fairly accurate prediction (5-20% error) of relative intensities of the two loss peaks for various isotope mixing ratios. This result again strongly supports the CCH model but cannot be reconciled with the benzene model or other polymerization products.

4. Conclusions

The high-resolution EELS data discussed in Sec. 3 provides rather clear spectral evidence for CCH formation from C_2H_2 on both (111) and (100) palladium surfaces. Although this species was interpreted as CH in earlier work on Pd(111) [2] the present investigation strongly favors the CCH model since the band attributable to ν_{CC} is consistently found on the (100) surface. Furthermore, an appealing aspect of room-temperature CCH formation on Pd(111) is the release of hydrogen necessary to also form the $\equiv C-CH_3$ species from acetylene. This is the first clear evidence for such a species on (100) and (111) surfaces of Pd or related metals although a CCH species was proposed on Ni(110) in UPS studies [17]. In this regard it may be important to reconsider the earlier assignments made to CH species on Ni, Pt, and Rh [10] in terms of CCH formation due to the close resemblance of the various spectra.

Evidently CCH stereochemistry on palladium involves bonding of both carbon atoms to the metal surface leading to a C-C bond order between 1 and 2 judging from the present EELS results. We postulate that a likely bonding geometry involves the C-C axis parallel or slightly skewed to the surface, consistent with a strong CH bending loss and a weak loss due to the CC stretch. These general features would not be sensitive to structural details on the (100) and (111) surfaces.

We also note the high stability of the CCH species. Thermal processing measurements on Pd(100) indicate that decomposition begins only after ~550K and ~30% of the original species remains at 650K. In this regard, ab initio calculations on CCH bonding geometry and relative stability compared to C_2H_2, CH, etc., would be of considerable interest.

Acknowledgments

We are grateful to Dr. J.E. Demuth for his interest in this work and for numerous stimulating discussions. We thank Drs. G. Ertl, R.M. Lambert, and E.L. Muetterties for kindly providing preprints of their work prior to publication. We also thank Mr. Hye Keun O for his able technical assistance. This work was supported by the Office of Naval Research.

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[16] We find a mode of medium intensity ca.830 cm^{-1} for C_6D_6 on Pd(111); a similar mode was reported on Rh(111) [13].

[17] J.E. Demuth, Surface Sci. 93 (1980) 127.

Figure Captions

Fig. 1: High-resolution EELS spectra for hydrocarbon adsorption on Pd(100).

(a) 10L C_2H_2 exposure at 300K

(b) Thermal processing of (a) to 450K

(c) 2L C_6H_6 exposure at 300K

Scale changes refer to the elastic beam for each panel in this and subsequent figures.

Fig. 2: High-resolution EELS spectra for hydrocarbon adsorption on Pd(111).

acetylene: (a) 3 L exposure at 150K,

(b) 1.5 L exposure at 300K,

(c) 12 L exposure at 300K,

(d) Thermal processing of (c) to 500K

benzene: (e) 1 L exposure at 300K, warmed to 450K.

Fig. 3: Comparison of high-resolution EELS spectra for the 475K acetylene-derived surface phase and benzene for off-specular scattering on Pd(100).

Fig. 4: High-resolution EELS spectra due to mixing of C_6H_6 and D_2 on Pd(111). Lines labeled A-D show the predicted positions for various benzene isotopes due to the ν_4 modes (see text). Positions of sym-$C_6H_3D_3$, para-$C_6H_4D_2$, and para-$C_6H_2D_4$ are shown. The additional ortho-, meta-$C_6H_4D_2$, 1,2,3-$C_6H_3D_3$, etc., isotopes

are slightly shifted from the respective groupings shown [15]. Information on the C_6HD_5 isotope was not found for this mode.

Fig. 5: High-resolution EELS spectra due to isotope mixing of C_2H_2 and C_2D_2 on Pd(100).

(a) 300K spectrum due to co-adsorbed C_2H_2 and C_2D_2.

(b) Thermal processing of (a) to 450K leads to CCH, CCD spectrum. Dashed lines indicate predicted isotope vibrational losses in the event of benzene formation (cf. Fig. 4).

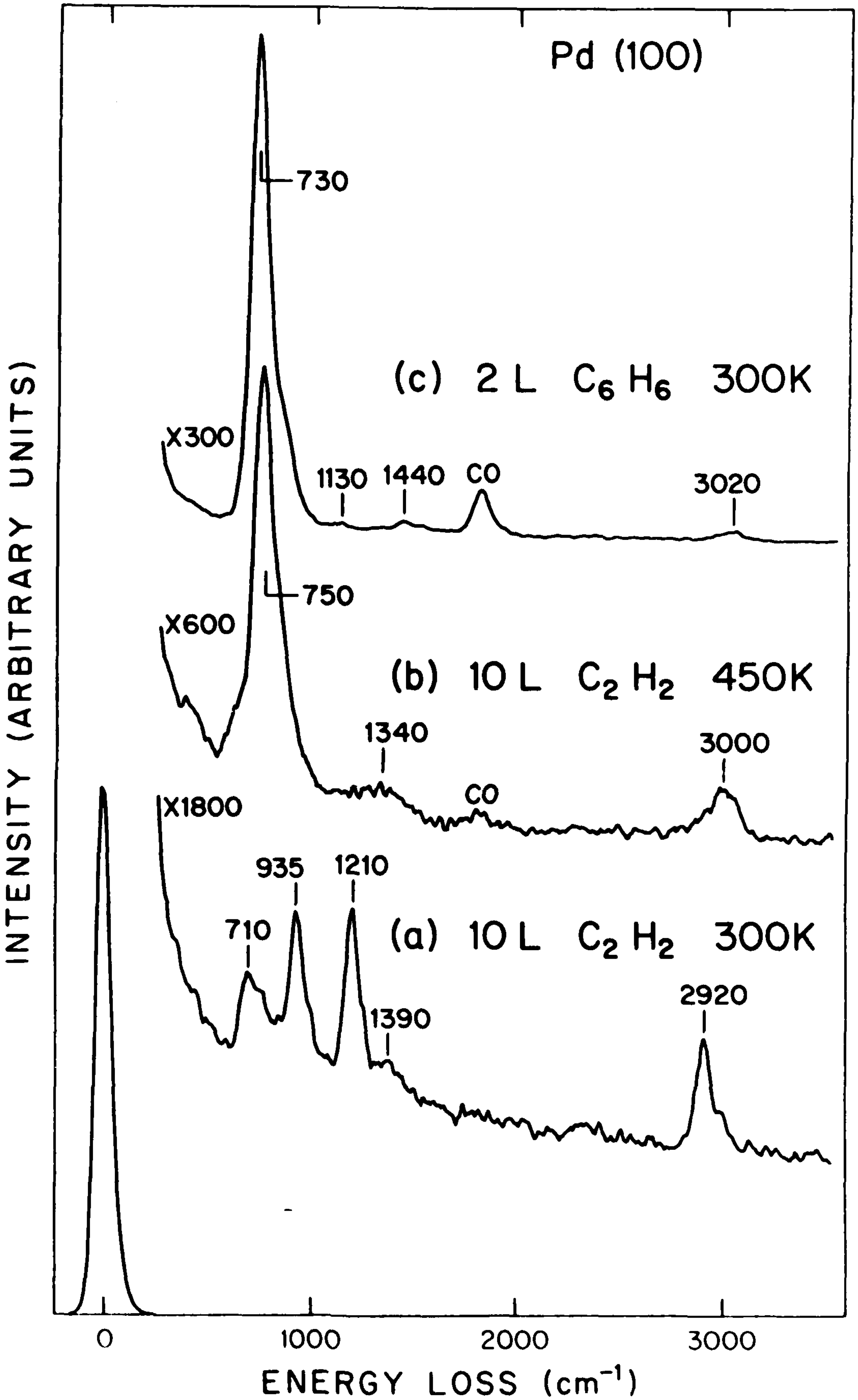
Pd (100)
(c) 2 L C_6H_6 300K
X300
730
1130
1440
CO
3020
(b) 10 L C_2H_2 450K
X600
750
1340
CO
3000
(a) 10 L C_2H_2 300K
X1800
710
935
1210
1390
2920
INTENSITY (ARBITRARY UNITS)
0
1000
2000
3000
ENERGY LOSS (cm^{-1})

Fig. 1

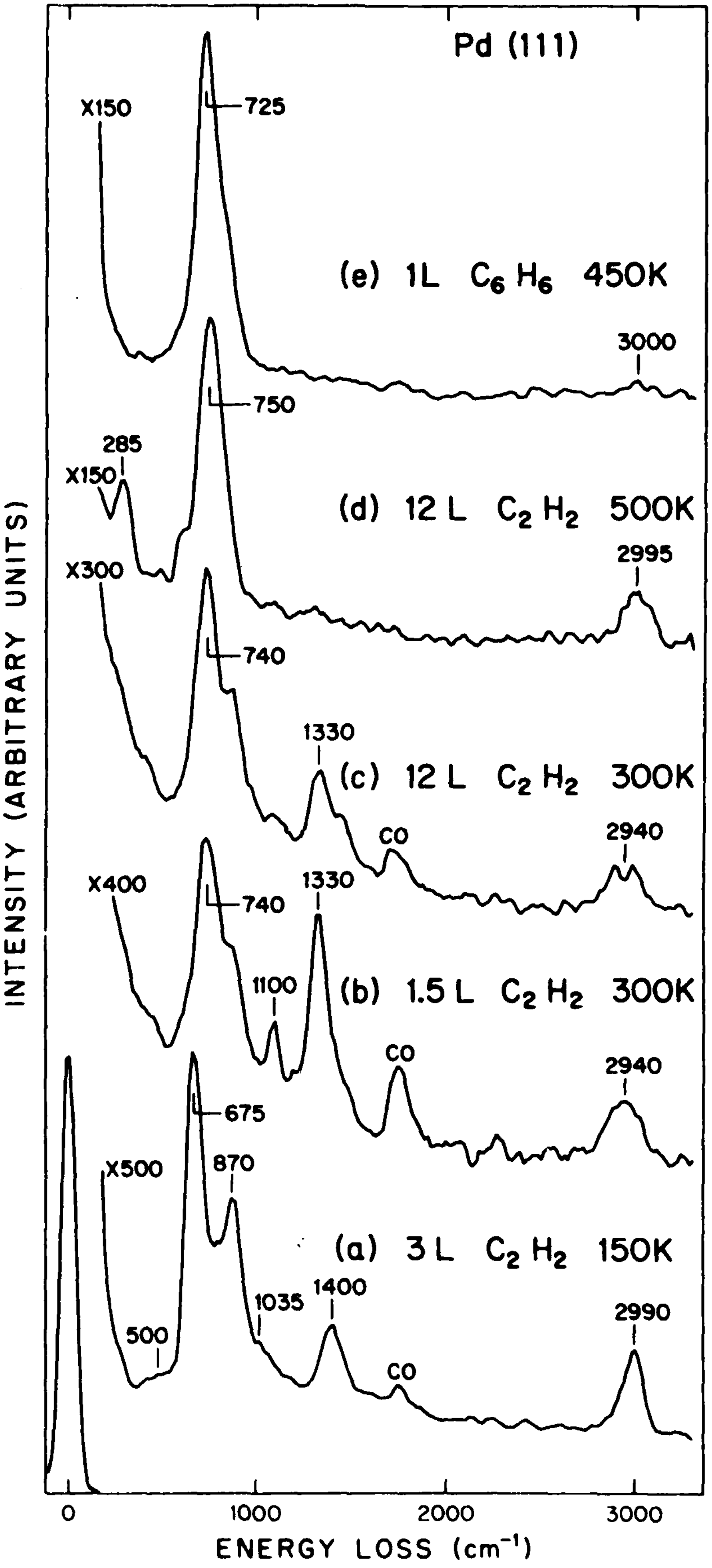
Pd (111)
X150
725
(e) 1L C_6H_6 450K
3000
750
285
X150
(d) 12 L C_2H_2 500K
2995
X300
740
1330
(c) 12 L C_2H_2 300K
CO
2940
X400
740
1330
1100
(b) 1.5 L C_2H_2 300K
CO
2940
675
X500
870
(a) 3 L C_2H_2 150K
1035
1400
500
CO
2990
INTENSITY (ARBITRARY UNITS)
0
1000
2000
3000
ENERGY LOSS (cm^{-1})

Fig. 2

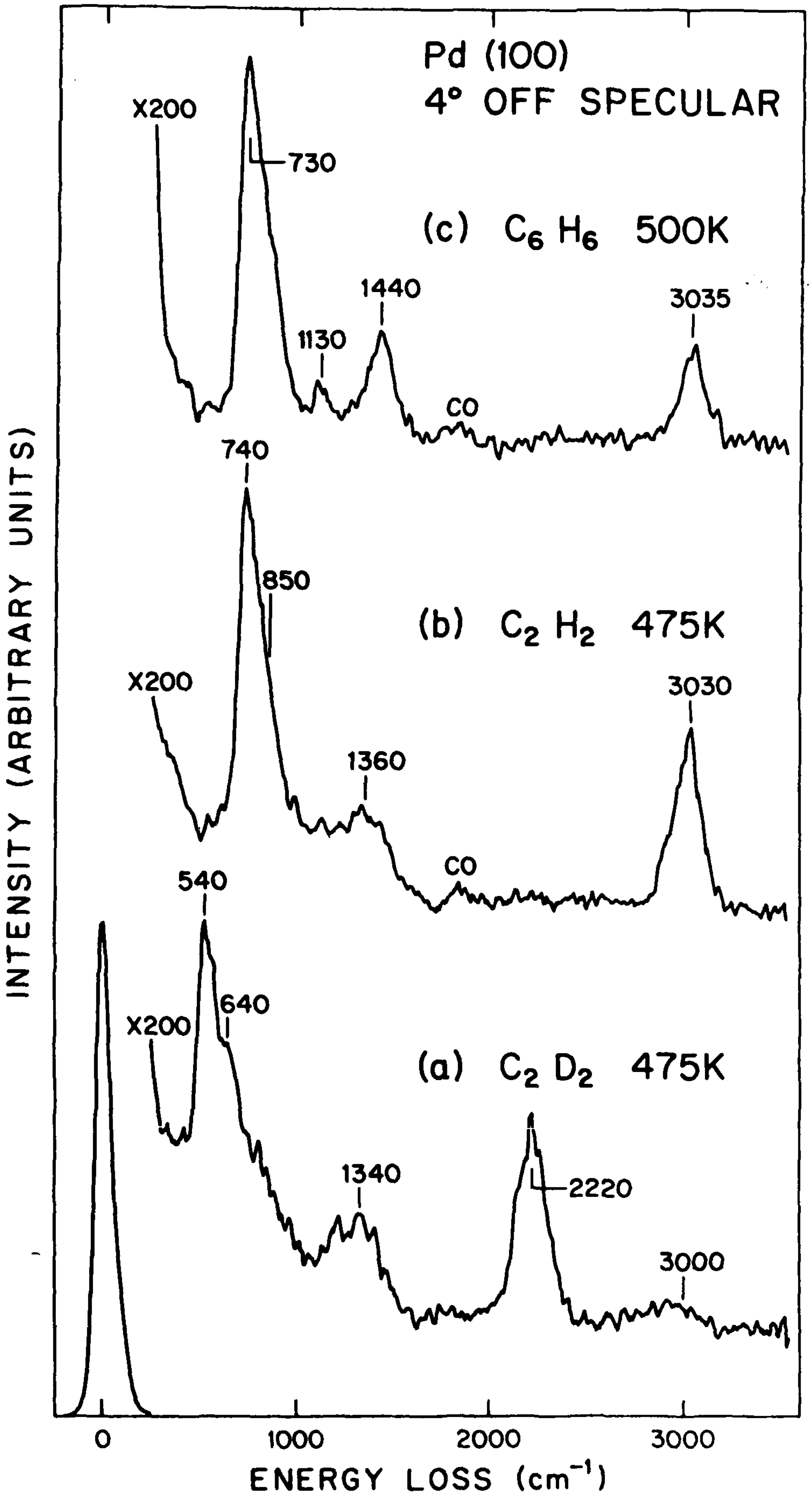
Pd (100)
4° OFF SPECULAR
X200
730
(c) C6 H6 500K
1440
1130
3035
CO
740
850
(b) C2 H2 475K
X200
3030
1360
CO
540
640
X200
(a) C2 D2 475K
1340
2220
3000
INTENSITY (ARBITRARY UNITS)
0
1000
2000
3000
ENERGY LOSS (cm-1)

Fig. 3

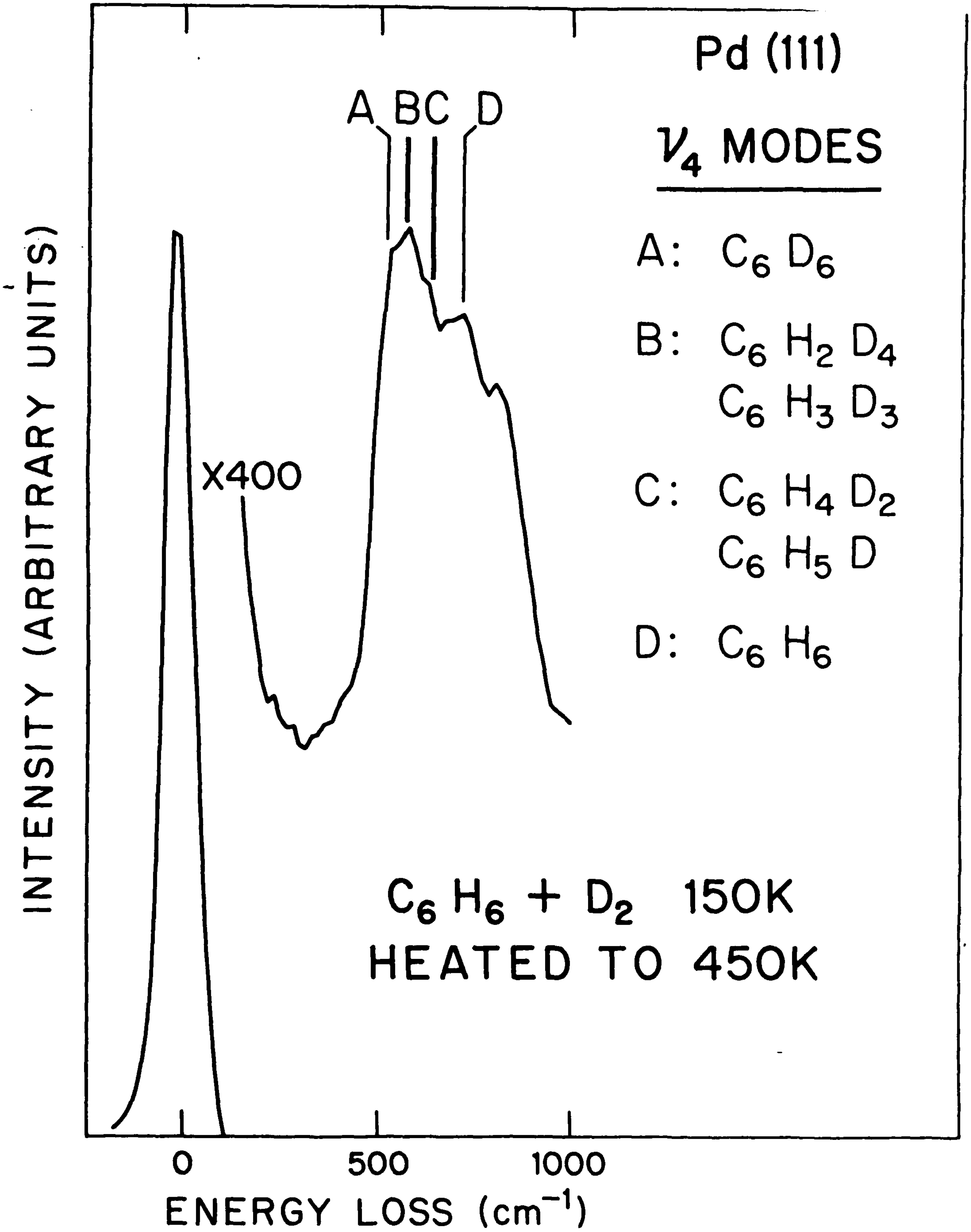
Pd (111)
ν_4 MODES
A: C_6D_6
B: $C_6H_2D_4$
$C_6H_3D_3$
C: $C_6H_4D_2$
C_6H_5D
D: C_6H_6
A
B
C
D
X400
$C_6H_6 + D_2$ 150K
HEATED TO 450K
INTENSITY (ARBITRARY UNITS)
0
500
1000
ENERGY LOSS (cm^{-1})

Fig. 4

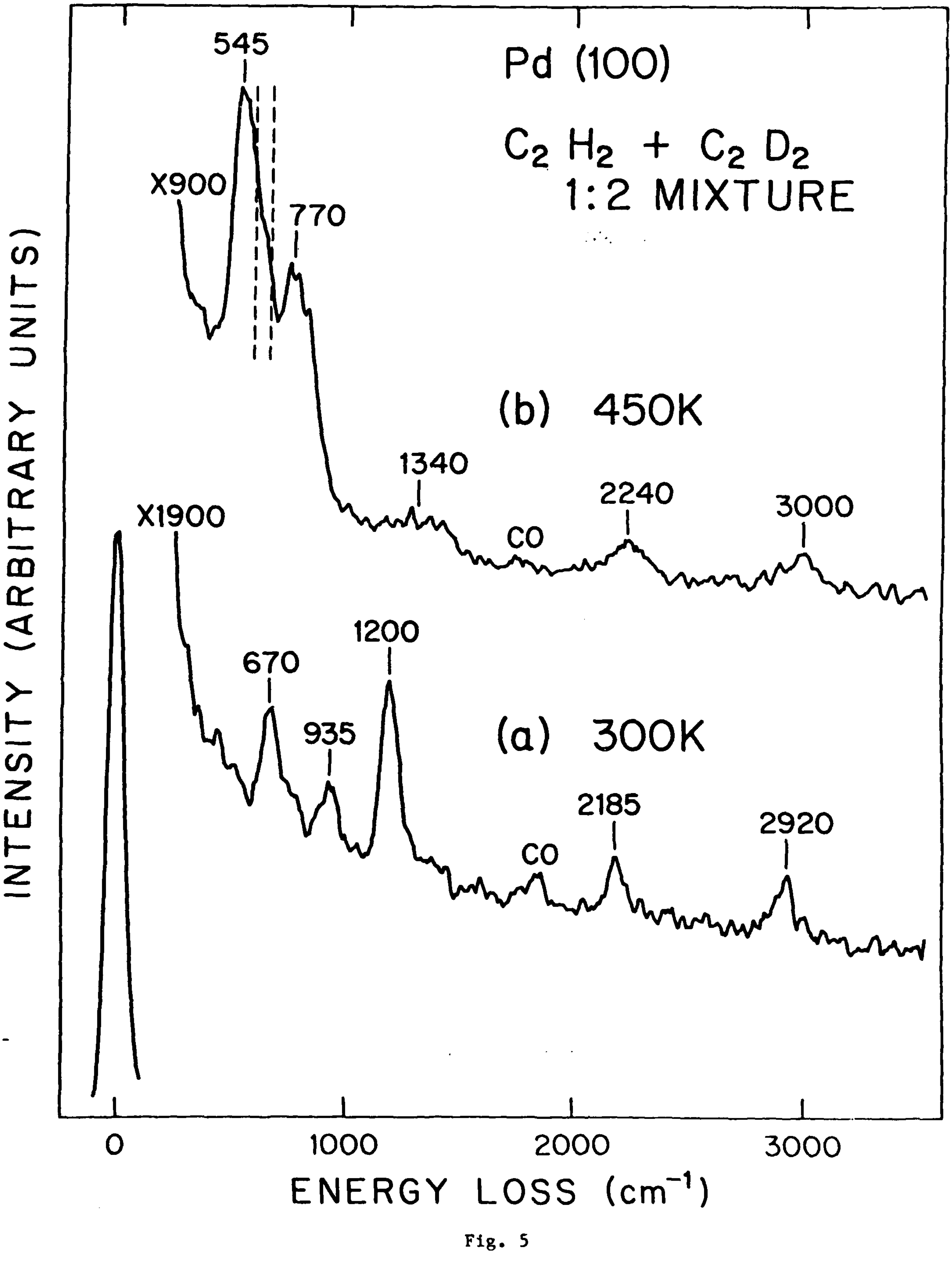
Pd (100)
$C_2H_2 + C_2D_2$
1:2 MIXTURE
545
X900
770
(b) 450K
1340
CO
2240
3000
X1900
1200
670
935
(a) 300K
2185
2920
CO
INTENSITY (ARBITRARY UNITS)
0
1000
2000
3000
ENERGY LOSS (cm^{-1})

Fig. 5